

027



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ : C10L 1/18, 10/00, C07C 43/11, 43/18, 43/20, 69/00, 69/76</p>	<p>A1</p>	<p>(11) International Publication Number: WO 94/14925 (43) International Publication Date: 7 July 1994 (07.07.94)</p>
<p>(21) International Application Number: PCT/US93/12320 (22) International Filing Date: 17 December 1993 (17.12.93) (30) Priority Data: 07/992,953 18 December 1992 (18.12.92) US (71) Applicant: CHEVRON RESEARCH AND TECHNOLOGY COMPANY, a division [US/US]; of CHEVRON U.S.A., INC., P.O. Box 7141, San Francisco, CA 94120-7141 (US). (72) Inventor: CHERPECK, Richard, E.; 8962 Cypress Avenue, Cotati, CA 94931 (US). (74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Department, P.O. Box 7141, San Francisco, CA 94120-7141 (US).</p>		<p>(81) Designated States: AU, BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.</p>
<p>(54) Title: POLY(OXYALKYLENE) HYDROXYAROMATIC ETHERS AND FUEL COMPOSITIONS CONTAINING THE SAME</p>		
<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> <p>(I)</p> </div> <div style="text-align: center;"> <p>(II)</p> </div> </div>		
<p>(57) Abstract</p> <p>Poly(oxyalkylene) hydroxyaromatic ethers having formula (I) or a fuel-soluble salt thereof; where R₁ and R₂ are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms; R₃ and R₄ are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms; R₅ is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group of formula (II) where R₆ is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms; n is an integer from 5 to 100; and x is an integer from 0 to 10. The poly(oxyalkylene) hydroxyaromatic ethers of formula (I) are useful as fuel additives for the prevention and control of engine deposits.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

-1-

POLY(OXYALKYLENE) HYDROXYAROMATIC ETHERS
AND FUEL COMPOSITIONS CONTAINING THE SAME

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to novel hydroxyaromatic compounds. More particularly, this invention relates to novel poly(oxyalkylene) hydroxyaromatic ethers and their use in fuel compositions to prevent and control engine deposits.

Description of the Related Art

It is well known that automobile engines tend to form deposits on the surface of engine components, such as carburetor ports, throttle bodies, fuel injectors, intake ports and intake valves, due to the oxidation and polymerization of hydrocarbon fuel. These deposits, even when present in relatively minor amounts, often cause noticeable driveability problems, such as stalling and poor acceleration. Moreover, engine deposits can significantly increase an automobile's fuel consumption and production of exhaust pollutants. Therefore, the development of effective fuel detergents or "deposit control" additives to prevent or control such deposits is of considerable importance and numerous such materials are known in the art.

For example, aliphatic hydrocarbon-substituted phenols are known to reduce engine deposits when used in fuel compositions. U.S. Patent No. 3,849,085, issued November 19, 1974 to Kreuz et al., discloses a motor fuel composition comprising a mixture of hydrocarbons in the gasoline boiling range containing about 0.01 to 0.25 volume percent of a high molecular weight aliphatic hydrocarbon-substituted phenol in

-2-

01 which the aliphatic hydrocarbon radical has an average
02 molecular weight in the range of about 500 to 3,500. This
03 patent teaches that gasoline compositions containing minor
04 amount of an aliphatic hydrocarbon-substituted phenol not
05 only prevent or inhibit the formation of intake valve and
06 port deposits in a gasoline engine, but also enhance the
07 performance of the fuel composition in engines designed to
08 operate at higher operating temperatures with a minimum of
09 decomposition and deposit formation in the manifold of the
10 engine.

11
12 Similarly, U.S. Patent No. 4,134,846, issued January 16,
13 1979 to Machleder et al., discloses a fuel additive
14 composition comprising a mixture of (1) the reaction product
15 of an aliphatic hydrocarbon-substituted phenol,
16 epichlorohydrin and a primary or secondary mono- or
17 polyamine, and (2) a polyalkylene phenol. This patent
18 teaches that such compositions show excellent carburetor,
19 induction system and combustion chamber detergency and, in
20 addition, provide effective rust inhibition when used in
21 hydrocarbon fuels at low concentrations.

22
23 Fuel additives containing a poly(oxyalkylene) moiety are
24 also known in the art. For example, U.S. Patent No.
25 4,191,537, issued March 4, 1980 to R. A. Lewis et al.,
26 discloses a fuel composition comprising a major portion of
27 hydrocarbons boiling in the gasoline range and from 30 to
28 2000 ppm of a hydrocarbyl poly(oxyalkylene) aminocarbamate
29 having a molecular weight from about 600 to 10,000, and at
30 least one basic nitrogen atom. The hydrocarbyl
31 poly(oxyalkylene) moiety is composed of oxyalkylene units
32 selected from 2 to 5 carbon oxyalkylene units. These fuel
33 compositions are taught to maintain the cleanliness of
34 intake systems without contributing to combustion chamber
35 deposits.

-3-

01 Aromatic compounds containing a poly(oxyalkylene) moiety are
02 also known in the art. For example, the above-mentioned
03 U.S. Patent No. 4,191,537, discloses alkylphenyl
04 poly(oxyalkylene) polymers which are useful as intermediates
05 in the preparation of alkylphenyl poly(oxyalkylene)
06 aminocarbamates.

07

08 Additionally, hydroxyaromatic compounds containing a
09 poly(oxyalkylene) moiety are known in the art. For example,
10 U.S. Patent No. 4,952,732, issued August 28, 1990 to G. P.
11 Speranza et al., discloses Mannich condensates prepared from
12 a phenol, formaldehyde and an alkylamine containing propoxy
13 groups and, optionally, ethoxy groups. These Mannich
14 condensates are taught to be useful as corrosion inhibitors,
15 water repellent agents, paint adhesion promoters, and also
16 as intermediates for preparing surfactants, and pololys
17 finding use in the manufacture of polyurethane foam.

18

19 It has now been discovered that certain hydroxyaromatic
20 ethers having a poly(oxyalkylene) "tail" provide excellent
21 control of engine deposits, especially intake valve
22 deposits, when employed as fuel additives in fuel
23 compositions. Moreover, these poly(oxyalkylene)
24 hydroxyaromatic ethers have been found to produce fewer
25 combustion chamber deposits than known aliphatic
26 hydrocarbon-substituted phenolic fuel additives.

27

28

29

SUMMARY OF THE INVENTION

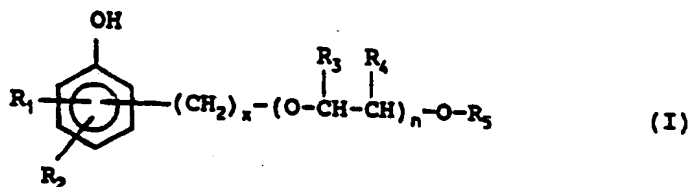
30

31 The present invention provides novel poly(oxyalkylene)
32 hydroxyaromatic ethers which are useful as fuel additives
33 for the prevention and control of engine deposits,
34 particularly intake valve deposits.

35

-4-

01 The poly(oxyalkylene) hydroxyaromatic ethers of the present
 02 invention have the formula:



11 or a fuel-soluble salt thereof; wherein R_1 and R_2 are each
 12 independently hydrogen, hydroxy, lower alkyl having 1 to 6
 13 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;
 14 R_3 and R_4 are each independently hydrogen or lower alkyl
 15 having 1 to 6 carbon atoms; R_5 is hydrogen, alkyl having 1
 16 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to
 17 36 carbon atoms, or an acyl group of the formula:



22
 23 wherein R_6 is alkyl having 1 to 30 carbon atoms, phenyl, or
 24 aralkyl or alkaryl having 7 to 36 carbon atoms; n is an
 25 integer from 5 to 100; and x is an integer from 0 to 10.

26
 27 The present invention further provides a fuel composition
 28 comprising a major amount of hydrocarbons boiling in the
 29 gasoline or diesel range and an effective deposit-
 30 controlling amount of a hydroxyaromatic poly(oxyalkylene)
 31 ether of the present invention.

32
 33 The present invention additionally provides a fuel
 34 concentrate comprising an inert stable oleophilic organic
 35 solvent boiling in the range of from about 150°F to 400°F

-5-

01 and from about 10 to 70 weight percent of a hydroxyaromatic
 02 poly(oxyalkylene) ether of the present invention.

03

04 Among other factors, the present invention is based on the
 05 surprising discovery that certain poly(oxyalkylene)
 06 hydroxyaromatic ethers, when employed as fuel additives in
 07 fuel compositions, provide excellent control of engine
 08 deposits, especially on intake valves, and produce fewer
 09 combustion chamber deposits than known aliphatic
 10 hydrocarbon-substituted phenolic fuel additives.

11

12

13

DETAILED DESCRIPTION OF THE INVENTION

14

15 The fuel additives provided by the present invention have
 16 the general formula:

17

18

19

20

21

22

23

24

25 or a fuel-soluble salt thereof; wherein R_1 , R_2 , R_3 , R_4 , R_5 , n
 26 and x are as defined hereinabove.

27

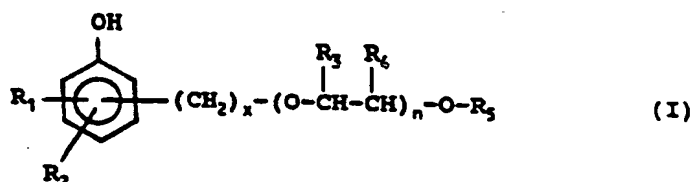
28 Preferably, R_1 is hydrogen, hydroxy, or lower alkyl having 1
 29 to 4 carbon atoms. More preferably, R_1 is hydrogen or
 30 hydroxy. Most preferably, R_1 is hydrogen.

31

32 R_2 is preferably hydrogen.

33

34 Preferably, one of R_3 and R_4 is lower alkyl having 1 to 3
 35 carbon atoms and the other is hydrogen. More preferably,



-5-

01 and from about 10 to 70 weight percent of a hydroxyaromatic
 02 poly(oxyalkylene) ether of the present invention.

03

04 Among other factors, the present invention is based on the
 05 surprising discovery that certain poly(oxyalkylene)
 06 hydroxyaromatic ethers, when employed as fuel additives in
 07 fuel compositions, provide excellent control of engine
 08 deposits, especially on intake valves, and produce fewer
 09 combustion chamber deposits than known aliphatic
 10 hydrocarbon-substituted phenolic fuel additives.

11

12

13

DETAILED DESCRIPTION OF THE INVENTION

14

15 The fuel additives provided by the present invention have
 16 the general formula:

17

18

19

20

21

22

23

24

25 or a fuel-soluble salt thereof; wherein R_1 , R_2 , R_3 , R_4 , R_5 , n
 26 and x are as defined hereinabove.

27

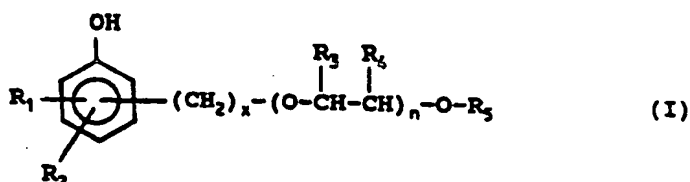
28 Preferably, R_1 is hydrogen, hydroxy, or lower alkyl having 1
 29 to 4 carbon atoms. More preferably, R_1 is hydrogen or
 30 hydroxy. Most preferably, R_1 is hydrogen.

31

32 R_2 is preferably hydrogen.

33

34 Preferably, one of R_3 and R_4 is lower alkyl having 1 to 3
 35 carbon atoms and the other is hydrogen. More preferably,



-6-

01 one of R_3 and R_4 is methyl or ethyl and the other is
02 hydrogen. Most preferably, one of R_3 and R_4 is ethyl and
03 the other is hydrogen.

04

05 R_5 is preferably hydrogen, alkyl having 2 to 22 carbon
06 atoms, alkylphenyl having an alkyl group containing 4 to 24
07 carbon atoms, or an acyl group having the formula: $-C(O)R_7$,
08 wherein R_7 is alkyl having 4 to 12 carbon atoms. More
09 preferably, R_5 is hydrogen, alkyl having 4 to 12 carbon
10 atoms, or alkylphenyl having an alkyl group containing 4 to
11 12 carbon atoms. Most preferably, R_5 is hydrogen.

12

13 Preferably, n is an integer from 10 to 50. More preferably,
14 n is an integer from 15 to 30. Preferably, x is an integer
15 from 0 to 2. More preferably, x is 0.

16

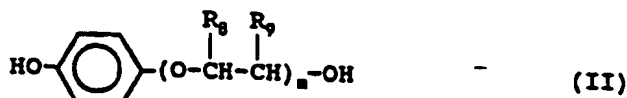
17 A preferred group of poly(oxyalkylene) hydroxyaromatic
18 ethers are those of formula I wherein R_1 is hydrogen,
19 hydroxy, or lower alkyl having 1 to 4 carbon atoms; R_2 is
20 hydrogen; one of R_3 and R_4 is hydrogen and the other is
21 methyl or ethyl; R_5 is hydrogen, alkyl having 4 to 12 carbon
22 atoms, alkylphenyl having an alkyl group containing 4 to 12
23 carbon atoms, or an acyl group having the formula: $-C(O)R_7$,
24 wherein R_7 is alkyl having 4 to 12 carbon atoms; n is 15 to
25 30 and x is 0.

26

27 Another preferred group of poly(oxyalkylene) hydroxyaromatic
28 ethers are those of formula I wherein R_1 is hydrogen,
29 hydroxy, or lower alkyl having 1 to 4 carbon atoms; R_2 is
30 hydrogen; one of R_3 and R_4 is hydrogen and the other is
31 methyl or ethyl; R_5 is hydrogen, alkyl having 4 to 12 carbon
32 atoms, alkylphenyl having an alkyl group containing 4 to 12
33 carbon atoms, or an acyl group having the formula: $-C(O)R_7$,
34 wherein R_7 is alkyl having 4 to 12 carbon atoms; n is 15 to
35 30 and x is 1 or 2.

01 A more preferred group of poly(oxyalkylene) hydroxyaromatic
02 ethers are those of formula I wherein R_1 is hydrogen or
03 hydroxy; R_2 is hydrogen; one of R_3 and R_4 is hydrogen and the
04 other is methyl or ethyl; R_5 is hydrogen, alkyl having 4 to
05 12 carbon atoms, or alkylphenyl having an alkyl group
06 containing 4 to 12 carbon atoms; n is 15 to 30; and x is 0.
07

08 A particularly preferred group of poly(oxyalkylene)
09 hydroxyaromatic ethers are those having the formula:
10



15 wherein one of R_8 and R_9 is methyl or ethyl and the other is
16 hydrogen; and m is an integer from 15 to 30.

17 The poly(oxyalkylene) hydroxyaromatic ethers of the present
18 invention will generally have a sufficient molecular weight
19 so as to be non-volatile at normal engine intake valve
20 operating temperatures (about 200-250°C). Typically, the
21 molecular weight of the poly(oxyalkylene) hydroxyaromatic
22 ethers of this invention will range from about 600 to about
23 10,000, preferably from 1,000 to 3,000.
24

25 Generally, the poly(oxyalkylene) hydroxyaromatic ethers of
26 this invention will contain an average of about 5 to about
27 100 oxyalkylene units; preferably, 10 to 50 oxyalkylene
28 units; more preferably, 15 to 30 oxyalkylene units.
29

30 Fuel-soluble salts of the poly(oxyalkylene) hydroxyaromatic
31 ethers of the present invention are also contemplated to be
32 useful for preventing or controlling deposits. Such salts
33 include alkali metal, alkaline earth metal, ammonium,
34 substituted ammonium and sulfonium salts. Preferred metal
35

-8-

01 salts are the alkali metal salts, particularly the sodium
02 and potassium salts, and the substituted ammonium salts,
03 particularly tetraalkyl-substituted ammonium salts, such as
04 the tetrabutylammonium salts.

05

06 Definitions

07

08 As used herein the following terms have the following
09 meanings unless expressly stated to the contrary.

10

11 The term "alkyl" refers to both straight- and branched-chain
12 alkyl groups.

13

14 The term "lower alkyl" refers to alkyl groups having 1 to
15 about 6 carbon atoms and includes primary, secondary and
16 tertiary alkyl groups. Typical lower alkyl groups include,
17 for example, methyl, ethyl, n-propyl, isopropyl, n-butyl,
18 sec-butyl, t-butyl, n-pentyl, n-hexyl and the like.

19

20 The term "lower alkoxy" refers to the group $-OR_x$ wherein R_x
21 is lower alkyl. Typical lower alkoxy groups include
22 methoxy, ethoxy, and the like.

23

24 The term "alkaryl" refers to the group:

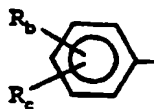
25

26

27

28

29



30 wherein R_b and R_c are each independently hydrogen or an
31 alkyl group, with the proviso that both R_b and R_c are not
32 hydrogen. Typical alkaryl groups include, for example,
33 tolyl, xylyl, cumenyl, ethylphenyl, butylphenyl,
34 dibutylphenyl, hexylphenyl, octylphenyl, dioctylphenyl,
35 nonylphenyl, decylphenyl, didecylphenyl, dodecylphenyl,

-9-

01 hexadecylphenyl, octadecylphenyl, icosylphenyl,
 02 tricontylphenyl and the like. The term "alkylphenyl" refers
 03 to an alkaryl group of the above formula in which R_b is
 04 alkyl and R_c is hydrogen.

05

06 The term "aralkyl" refers to the group:

07

08

09

10

11



12 wherein R_d and R_e are each independently hydrogen or an
 13 alkyl group; and R_f is an alkylene group. Typical alkaryl
 14 groups include, for example, benzyl, methylbenzyl,
 15 dimethylbenzyl, phenethyl, and the like.

16

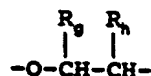
17 The term "oxyalkylene unit" refers to an ether moiety having
 18 the general formula:

19

20

21

22



23 wherein R_g and R_h are each independently hydrogen or lower
 24 alkyl groups.

25

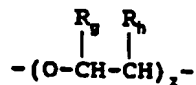
26 The term "poly(oxyalkylene)" refers to a polymer or oligomer
 27 having the general formula:

28

29

30

31



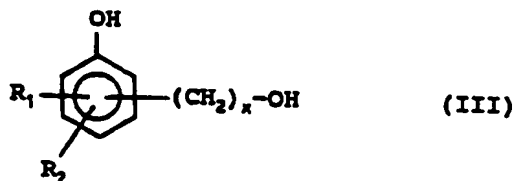
32 wherein R_g and R_h are as defined above, and z is an integer
 33 greater than 1. When referring herein to the number of
 34 poly(oxyalkylene) units in a particular poly(oxyalkylene)
 35

01 compound, it is to be understood that this number refers to
02 the average number of poly(oxyalkylene) units in such
03 compounds unless expressly stated to the contrary.
04

05 General Synthetic Procedures
06

07 The poly(oxyalkylene) hydroxyaromatic ethers of this
08 invention may be prepared by the following general methods
09 and procedures. It should be appreciated that where typical
10 or preferred process conditions (e.g. reaction temperatures,
11 times, mole ratios of reactants, solvents, pressures, etc.)
12 are given, other process conditions may also be used unless
13 otherwise stated. Optimum reaction conditions may vary with
14 the particular reactants or solvents used, but such
15 conditions can be determined by one skilled in the art by
16 routine optimization procedures.
17

18 The poly(oxyalkylene) hydroxyaromatic ethers of the present
19 invention may be prepared from a hydroxyaromatic compound
20 having the formula:
21



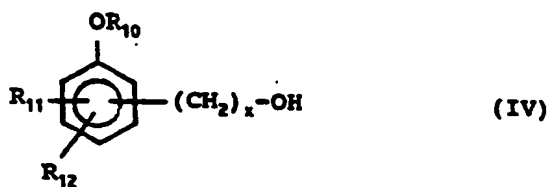
29 wherein R_1 , R_2 , and x are as defined above.
30

31 The hydroxyaromatic compounds of formula III are either
32 known compounds or can be prepared from known compounds by
33 conventional procedures. Suitable hydroxyaromatic compounds
34 for use as starting materials in this invention include
35 catechol, resorcinol, hydroquinone, 1,2,3-trihydroxybenzene

-11-

01 (pyrogallol), 1,2,4-trihydroxybenzene (hydroquinol), 1,3,5-
 02 trihydroxybenzene (phloroglucinol), 1,4-dihydroxy-2-
 03 methylbenzene, 1,3-dihydroxy-5-methylbenzene, 2-t-butyl-1,4-
 04 dihydroxybenzene, 2,6-di-t-butyl-1,4-dihydroxybenzene, 1,4-
 05 dihydroxy-2-methoxybenzene, 1,3-dihydroxy-5-methoxybenzene,
 06 4-hydroxybenzyl alcohol, 4-hydroxyphenethyl alcohol and the
 07 like.

08
 09 In a preferred method of synthesizing the poly(oxyalkylene)
 10 hydroxyaromatic ethers of the present invention, a
 11 hydroxyaromatic compound of formula III is first selectively
 12 protected to provide a compound having the formula:



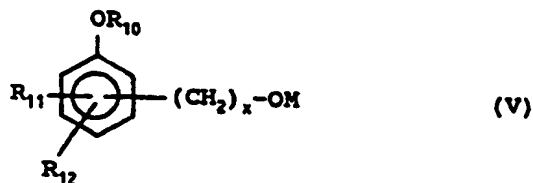
20
 21 wherein R_{10} is a suitable hydroxyl protecting group, such as
 22 benzyl, tert-butyldimethylsilyl, methoxymethyl, and the
 23 like; R_{11} and R_{12} are each independently hydrogen, lower
 24 alkyl, lower alkoxy, or the group $-OR_{13}$, wherein R_{13} is a
 25 suitable hydroxyl protecting group, such as benzyl, tert-
 26 butyldimethylsilyl, methoxymethyl, and the like.
 27 Preferably, R_{10} and R_{13} are benzyl; except in the case where
 28 x is 1, then R_{10} and R_{13} are preferably a tert-butyl-
 29 dimethylsilyl group.

30
 31 Selective protection of III may be accomplished using
 32 conventional procedures. The choice of a suitable
 33 protecting group for a particular hydroxyaromatic compound
 34 will be apparent to those skilled in the art. Various
 35 protecting groups, and their introduction and removal, are

-12-

described, for example, in T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, Second Edition, Wiley, New York, 1991, and references cited therein. Alternatively, the protected derivatives IV can be prepared from known starting materials other than the hydroxyaromatic compounds of formula III by conventional procedures. In some cases, the protected derivatives IV are commercially available, e.g. 4-benzyloxyphenol is commercially available from Aldrich Chemical Co., Milwaukee, Wisconsin 53233.

The protected hydroxyaromatic compound of formula IV is then deprotonated with a suitable base to provide a metal salt having the formula:



wherein R_{10} , R_{11} , R_{12} and x are as defined above; and M is a metal cation, such as lithium, sodium or potassium.

Generally, this deprotonation reaction will be effected by contacting IV with a strong base, such as sodium hydride, potassium hydride, sodium amide and the like, in an inert solvent, such as toluene, xylene and the like, under substantially anhydrous conditions at a temperature in the range from about $-10^{\circ}C$ to about $120^{\circ}C$ for about 0.25 to about 3 hours.

Metal salt V is generally not isolated, but is reacted *in situ* with about 5 to about 100 molar equivalents of an

-13-

01 alkylene oxide (an epoxide) having the formula:

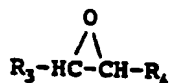
02

03

04

05

06



(VI)

07 wherein R_3 and R_4 are as defined above, to provide, after
08 neutralization, a poly(oxyalkylene) polymer or oligomer
09 having the formula:

10

11

12

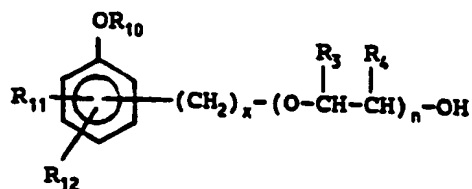
13

14

15

16

17



(VII)

18 wherein R_3 , R_4 , R_{10} , R_{11} , R_{12} , n and x are as defined above.

19

20 Typically, this polymerization reaction is conducted in a
21 substantially anhydrous inert solvent at a temperature of
22 about 30°C to about 150°C for about 2 to about 120 hours.
23 Suitable solvents for this reaction, include toluene, xylene
24 and the like. The reaction will generally be conducted at a
25 pressure sufficient to contain the reactants and the
26 solvent, preferably at atmospheric or ambient pressure.
27 More detailed reaction conditions for preparing
28 poly(oxyalkylene) compounds may be found in U.S. Patent Nos.
29 2,782,240 and 2,841,479, which are incorporated herein by
30 reference.

31

32 The amount of alkylene oxide employed in this reaction will
33 depend on the number of oxyalkylene units desired in the
34 product. Typically, the molar ratio of alkylene oxide VI to
35 metal salt V will range from about 5:1 to about 100:1;

-14-

01 preferably, from 10:1 to 50:1, more preferably from 15:1 to
02 30:1.

03

04 Suitable alkylene oxides for use in the polymerization
05 reaction include, for example, ethylene oxide; propylene
06 oxide; butylene oxides, such as 1,2-butylene oxide (1,2-
07 epoxybutane) and 2,3-butylene oxide (2,3-epoxybutane);
08 pentylene oxides; hexylene oxides; octylene oxides and the
09 like. Preferred alkylene oxides are propylene oxide and
10 1,2-butylene oxide.

11

12 In the polymerization reaction, a single type of alkylene
13 oxide may be employed, e.g. propylene oxide, in which case
14 the product is a homopolymer, e.g. a poly(oxypropylene).
15 However, copolymers are equally satisfactory and random
16 copolymers are readily prepared by contacting the metal salt
17 V with a mixture of alkylene oxides, such as a mixture of
18 propylene oxide and 1,2-butylene oxide, under polymerization
19 conditions. Copolymers containing blocks of oxyalkylene
20 units are also suitable for use in the present invention.
21 Block copolymers may be prepared by contacting the metal
22 salt V with first one alkylene oxide, then others in any
23 order, or repetitively, under polymerization conditions.

24

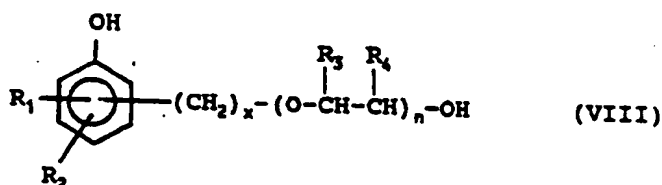
25 Poly(oxyalkylene) polymers of formula VII may also be
26 prepared by living or immortal polymerization as described
27 by S. Inoue and T. Aida in *Encyclopedia of Polymer Science*
28 *and Engineering*, Second Edition, Supplemental Volume, J.
29 Wiley and Sons, New York, pages 412-420 (1989). These
30 procedures are especially useful for preparing
31 poly(oxyalkylene) alcohols of formula V in which R_3 and R_4
32 are both alkyl groups.

33

34 Deprotection of the aromatic hydroxyl group(s) of VII using
35

-15-

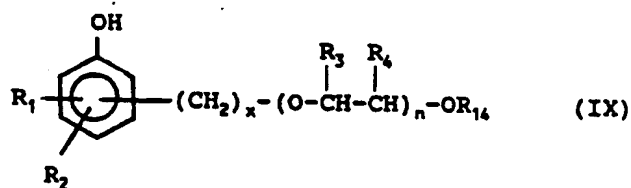
01 conventional procedures provides poly(oxyalkylene)
 02 hydroxyaromatic ethers of the present invention having the
 03 formula:



12 wherein R_1 - R_4 , n and x are as defined above.

13
 14 Appropriate conditions for this deprotection step will
 15 depend upon the protecting group(s) utilized in the
 16 synthesis and will be readily apparent to those skilled in
 17 the art. For example, benzyl protecting groups may be
 18 removed by hydrogenolysis under 1 to about 4 atmospheres of
 19 hydrogen in the presence of a catalyst, such as palladium on
 20 carbon. Typically, this deprotection reaction will be
 21 conducted in an inert solvent, preferably a mixture of ethyl
 22 acetate and acetic acid, at a temperature of from about 0°C
 23 to about 40°C for about 1 to about 24 hours.

24
 25 The poly(oxyalkylene) hydroxyaromatic ethers of the present
 26 invention containing an alkyl or alkaryl ether moiety, i.e.
 27 those having the formula:



34 wherein R_1 - R_4 , n and x are as defined above, and R_{14} is an
 35

01 alkyl group or aralkyl group, may be conveniently prepared
02 from a compound of formula VIII by selectively alkylating
03 the hydroxyl group of the poly(oxyalkylene) moiety of VIII
04 with a suitable alkylating agent.

05

06 Typically, this alkylation reaction will be conducted by
07 first contacting VIII with a sufficient amount of a strong
08 base capable of abstracting a proton from each the hydroxyl
09 groups present in VIII, including the aromatic hydroxyl
10 group(s) and the hydroxyl group of the poly(oxyalkylene)
11 moiety. Suitable bases for this reaction include, for
12 example, sodium hydride, potassium hydride, sodium amide and
13 the like. Generally, this deprotonation reaction will be
14 conducted in an inert solvent, such as toluene,
15 tetrahydrofuran, and the like, under substantially anhydrous
16 conditions at a temperature in the range from -10°C to 120°C
17 for about 0.25 to about 3 hours. The resulting metal salt
18 is then contacted with about 0.90 to about 1.1 molar
19 equivalents of a suitable alkylating agent at a temperature
20 in the range from 0°C to 120°C for about 1 to about 50 hours
21 to afford, after neutralization, a poly(oxyalkylene)
22 hydroxyaromatic ether of formula IX.

23

24 Suitable alkylating agents for use in this reaction include
25 alkyl and aralkyl halides, such as alkyl chlorides, bromides
26 and iodides and aralkyl chlorides, bromides and iodides; and
27 alkyl and aralkyl sulfonates, such as alkyl mesylates and
28 tosylates, and aralkyl mesylates and tosylates.

29

30 Preferred alkylating agents are primary and secondary alkyl
31 halides having 1 to 30 carbon atoms, and primary and
32 secondary aralkyl halides having 7 to 36 carbon atoms; more
33 preferred alkylating agents are primary alkyl halides having
34 4 to 12 carbon atoms.

35

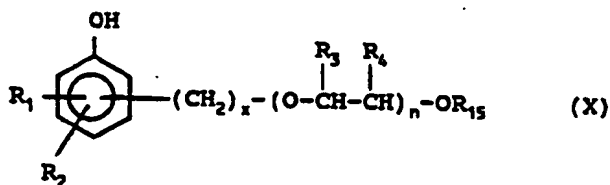
-17-

01 Representative examples of alkylating agents include, but
 02 are not limited to, methyl iodide, ethyl iodide, n-propyl
 03 bromide, n-butyl bromide, n-pentyl bromide, n-hexyl
 04 chloride, n-octyl chloride, n-decyl chloride, benzyl
 05 chloride and phenethyl chloride. Particularly preferred
 06 alkylating agents are benzyl chloride, n-butyl bromide.
 07

08 Alternatively, poly(oxyalkylene) hydroxyaromatic ethers of
 09 formula IX may be prepared by alkylating the hydroxyl group
 10 of the poly(oxyalkylene) moiety of protected intermediate
 11 VII, and then deprotecting the resulting product. The
 12 conditions for alkylating intermediate VII are essentially
 13 the same as those described above; however, a lesser amount
 14 of base will be required since the aromatic hydroxyl groups
 15 of VII are in a protected form.
 16

17 Other suitable methods for preparing alkyl and alkaryl
 18 ethers from alcohols, and appropriate reaction conditions
 19 for such reactions, can be found, for example, in I.T.
 20 Harrison and S. Harrison, *Compendium of Organic Synthetic*
 21 *Methods*, Vol. 1, pp. 310-312, Wiley-Interscience, New York
 22 (1971) and references cited therein.
 23

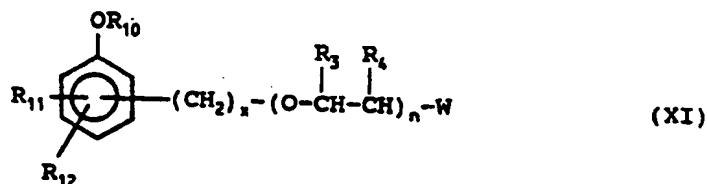
24 The poly(oxyalkylene) hydroxyaromatic ethers of the present
 25 invention containing an alkaryl ether moiety, i.e. those
 26 having the formula:
 27



34 wherein R_1 - R_4 , n and x are as defined above, and R_{15} is a
 35 phenyl or alkaryl group, may be prepared from intermediate

-18-

VII in several steps by first converting the hydroxyl group present of the poly(oxyalkylene) moiety of VII into a suitable leaving group, i.e. forming an intermediate having the formula:



wherein R_3 , R_4 , R_{10} , R_{11} , R_{12} , n and x are as defined above, and W is a suitable leaving group; and then displacing the leaving group of XI with a metal salt of a phenol having the formula:



wherein R_{16} and R_{17} are each independently hydrogen or an alkyl group. Subsequent deprotection of the resulting product affords poly(oxyalkylene) hydroxyaromatic ethers of formula X.

The hydroxyl group of the poly(oxyalkylene) moiety of VII may be converted into a suitable leaving group by contacting VII with a sulfonyl chloride to form a sulfonate ester, such as a methanesulfonate (mesylate) or a toluenesulfonate (tosylate). Typically, this reaction is conducted in the presence of a suitable amine, such as triethylamine or pyridine, in an inert solvent, such as dichloromethane, at a temperature in the range of about -10°C to about 30°C .

01 Alternatively, the hydroxyl group of the poly(oxyalkylene)
02 moiety of VII can be exchanged for a halide, such chloride
03 or bromide, by contacting VII with a halogenating agent,
04 such as thionyl chloride, oxalyl chloride or phosphorus
05 tribromide. Other suitable methods for preparing sulfonates
06 and halides from alcohols, and appropriate reaction
07 conditions for such reactions, can be found, for example, in
08 I.T. Harrison and S. Harrison, *Compendium of Organic*
09 *Synthetic Methods*, Vol. 1, pp. 331-337, Wiley-Interscience,
10 New York (1971) and references cited therein.
11

12 After forming intermediate XI, the leaving group may be
13 displaced therefrom by contacting XI with metal salt XII.
14 Generally, this reaction will be conducted in an inert
15 solvent, such as toluene, tetrahydrofuran and the like,
16 under substantially anhydrous conditions at a temperature in
17 the range of about 25°C to about 150°C for about 1 to about
18 48 hours. The metal salt XII can be formed by contacting
19 the corresponding phenol with a strong base capable of
20 abstracting the proton from the phenolic hydroxyl group,
21 such as sodium hydride, potassium hydride, sodium amide and
22 the like, in an inert solvent.
23

24 Suitable phenolic compounds for use in this reaction include
25 phenol, monoalkyl-substituted phenols and dialkyl-
26 substituted phenols. Monoalkyl-substituted phenols are
27 preferred, especially monoalkylphenols having an alkyl
28 substituent in the para position. Representative examples
29 of suitable phenolic compounds include, but are not limited
30 to, phenol, methylphenol, dimethylphenol, ethylphenol,
31 butylphenol, octylphenol, decylphenol, dodecylphenol,
32 tetradecylphenol, hexadecylphenol, octadecylphenol,
33 eicosylphenol, tetracosylphenol, hexacosylphenol,
34 triacontylphenol and the like. Also, mixtures of
35

01 alkylphenols may be employed, such as a mixture of C₁₄-C₁₈
 02 alkylphenols, a mixture of C₁₈-C₂₄ alkylphenols, a mixture of
 03 C₂₀-C₂₄ alkylphenols, or a mixture of C₁₆-C₂₆ alkylphenols.
 04

05 Particularly preferred alkylphenols are those derived from
 06 alkylation of phenol with polymers or oligomers of C₃ to C₆
 07 olefins, such as polypropylene or polybutene. These
 08 polymers preferably contain 10 to 30 carbon atoms. An
 09 especially preferred alkylphenol is prepared by alkylating
 10 phenol with a propylene polymer having an average of 4
 11 units. This polymer has the common name of propylene
 12 tetramer and is commercially available.
 13

14 Alternatively, the poly(oxyalkylene) hydroxyaromatic ethers
 15 of formula X can be prepared by displacing a leaving group
 16 from an intermediate having the formula:
 17



21
 22 wherein R₃, R₄, R₁₅, n and x are as defined above, and W is a
 23 suitable leaving group, with metal salt V; and then
 24 deprotecting the resulting product. Conditions for this
 25 reaction are essentially the same as those described above
 26 for reaction of XI with XII. Compounds of formula XIII may
 27 be prepared from XII and VI using the conditions described
 28 above for the preparation of VII, followed by conversion of
 29 the hydroxyl group of the poly(oxyalkylene) moiety of the
 30 resulting product into a suitable leaving using the
 31 procedures described above for the preparation of XI.
 32

33 The poly(oxyalkylene) hydroxyaromatic ethers of the present
 34 invention containing an acyl moiety, i.e those having the
 35

-21-

01 formula:

02

03

04

05

06

07

08

09

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

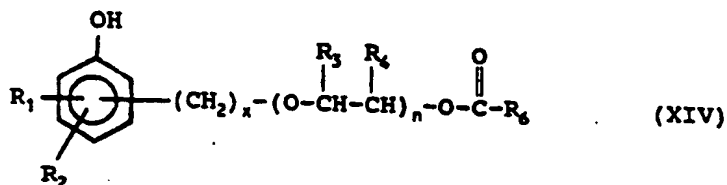
31

32

33

34

35



wherein R_1 -, R_2 -, R_3 -, R_4 -, R_6 -, n and x are as defined above; may be prepared from intermediate VII by first acylating the hydroxyl group of the poly(oxyalkylene) moiety of VII to form an ester. Subsequent deprotection of the aromatic hydroxyl group(s) of the resulting ester using conventional procedures then affords poly(oxyalkylene) hydroxyaromatic ethers of formula XIV.

Generally, the acylation reaction will be conducted by contacting intermediate VII with about 0.95 to about 1.2 molar equivalents of a suitable acylating agent. Suitable acylating agents for use in this reaction include acyl halides, such as acyl chlorides and bromides; and carboxylic acid anhydrides. Preferred acylating agents are those having the formula: $\text{R}_6\text{C(O)-X}$, wherein R_6 is alkyl having 1 to 30 carbon atom, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms, and X is chloro or bromo. More preferred acylating agents are those having the formula: $\text{R}_7\text{C(O)-X}$, wherein R_7 is alkyl having 4 to 12 carbon atoms. Representative examples of suitable acylating agents include, but are not limited to, acetyl chloride, acetic anhydride, propionyl chloride, butanoyl chloride, pivaloyl chloride, octanoyl chloride, decanoyl chloride 4-t-butylbenzoyl chloride and the like.

Generally, this reaction is conducted in an inert solvent,

-22-

01 such as toluene, dichloromethane, diethyl ether and the
02 like, at a temperature in the range of about 25°C to about
03 150°C, and is generally complete in about 0.5 to about 48
04 hours. When an acyl halide is employed as the acylating
05 agent, this reaction is preferably conducted in the presence
06 of a sufficient amount of an amine capable of neutralizing
07 the acid generated during the reaction, such as
08 triethylamine, di(isopropyl)ethylamine, pyridine or 4-
09 dimethylaminopyridine.

10
11 Additional methods for preparing esters from alcohols, and
12 suitable reaction conditions for such reactions, can be
13 found, for example, in I.T. Harrison and S. Harrison,
14 *Compendium of Organic Synthetic Methods*, Vol. 1, pp. 273-276
15 and 280-283, Wiley-Interscience, New York (1971) and
16 references cited therein.

17

18

19

Fuel Compositions

20 The poly(oxyalkylene) hydroxyaromatic ethers of the present
21 invention are useful as additives in hydrocarbon fuels to
22 prevent and control engine deposits, particularly intake
23 valve deposits. The proper concentration of additive
24 necessary to achieve the desired deposit control varies
25 depending upon the type of fuel employed, the type of
26 engine, and the presence of other fuel additives.

27

28 In general, the concentration of the poly(oxyalkylene)
29 hydroxyaromatic ethers of this invention in hydrocarbon fuel
30 will range from about 50 to about 2500 parts per million
31 (ppm) by weight, preferably from 75 to 1,000 ppm. When
32 other deposit control additives are present, a lesser amount
33 of the present additive may be used.

34

35

-23-

01 The poly(oxyalkylene) hydroxyaromatic ethers of the present
02 invention may be formulated as a concentrate using an inert
03 stable oleophilic (i.e., dissolves in gasoline) organic
04 solvent boiling in the range of about 150°F to 400°F (about
05 65°C to 205°C). Preferably, an aliphatic or an aromatic
06 hydrocarbon solvent is used, such as benzene, toluene,
07 xylene or higher-boiling aromatics or aromatic thinners.
08 Aliphatic alcohols containing about 3 to 8 carbon atoms,
09 such as isopropanol, isobutylcarbinol, n-butanol and the
10 like, in combination with hydrocarbon solvents are also
11 suitable for use with the present additives. In the
12 concentrate, the amount of the additive will generally range
13 from about 10 to about 70 weight percent, preferably 10 to
14 50 weight percent, more preferably from 20 to 40 weight
15 percent.

16
17 In gasoline fuels, other fuel additives may be employed with
18 the additives of the present invention, including, for
19 example, oxygenates, such as t-butyl methyl ether, antiknock
20 agents, such as methylcyclopentadienyl manganese
21 tricarbonyl, and other dispersants/detergents, such as
22 hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines, or
23 succinimides. Additionally, antioxidants, metal
24 deactivators and demulsifiers may be present.

25
26 In diesel fuels, other well-known additives can be employed,
27 such as pour point depressants, flow improvers, cetane
28 improvers, and the like.

29
30 A fuel-soluble, nonvolatile carrier fluid or oil may also be
31 used with the poly(oxyalkylene) hydroxyaromatic ethers of
32 this invention. The carrier fluid is a chemically inert
33 hydrocarbon-soluble liquid vehicle which substantially
34 increases the nonvolatile residue (NVR), or solvent-free
35 liquid fraction of the fuel additive composition while not

-24-

01 overwhelmingly contributing to octane requirement increase.
02 The carrier fluid may be a natural or synthetic oil, such as
03 mineral oil, refined petroleum oils, synthetic polyalkanes
04 and alkanes, including hydrogenated and unhydrogenated
05 polyalphaolefins, and synthetic polyoxyalkylene-derived
06 oils, such as those described, for example, in U.S. Patent
07 No. 4,191,537 to Lewis.

08
09 These carrier fluids are believed to act as a carrier for
10 the fuel additives of the present invention and to assist in
11 removing and retarding deposits. The carrier fluid may also
12 exhibit synergistic deposit control properties when used in
13 combination with the poly(oxyalkylene) hydroxyaromatic
14 ethers of this invention.

15
16 The carrier fluids are typically employed in amounts ranging
17 from about 100 to about 5000 ppm by weight of the
18 hydrocarbon fuel, preferably from 400 to 3000 ppm of the
19 fuel. Preferably, the ratio of carrier fluid to deposit
20 control additive will range from about 0.5:1 to about 10:1,
21 more preferably from 1:1 to 4:1, most preferably about 2:1.
22

23 When employed in a fuel concentrate, carrier fluids will
24 generally be present in amounts ranging from about 20 to
25 about 60 weight percent, preferably from 30 to 50 weight
26 percent.

27

28

EXAMPLES

29

30 The following examples are presented to illustrate specific
31 embodiments of the present invention and synthetic
32 preparations thereof; and should not be interpreted as
33 limitations upon the scope of the invention.

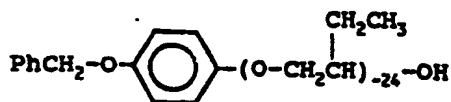
34

35

-25-

Example 1

Preparation of
 α -(4-Benzzyloxyphenyl)- ω -hydroxypoly(oxybutylene)

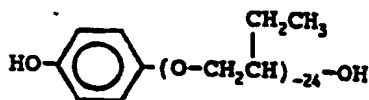


To a flask equipped with a magnetic stirrer, thermometer, addition funnel, reflux condenser and nitrogen inlet was added 6.88 grams of a 35 wt % dispersion of potassium hydride in mineral oil. Forty grams of 4-benzyloxyphenol dissolved in 500 mL of anhydrous toluene was added dropwise and the resulting mixture was stirred at room temperature for ten minutes. The temperature of the reaction mixture, a thick white suspension, was raised to 90°C and 430.8 mL of 1,2-epoxybutane was added dropwise. The reaction mixture was refluxed until the pot temperature reached 110°C (approximately 48 hours) at which time the reaction mixture was a light brown clear solution. The reaction was cooled to room temperature, quenched with 50 mL of methanol and diluted with 1 liter of diethyl ether. The resulting mixture was washed with saturated aqueous ammonium chloride, followed by water and saturated aqueous sodium chloride. The organic layer was dried over anhydrous magnesium sulfate, filtered and the solvents removed in vacuo to yield 390 grams of a yellow oil. The oil was chromatographed on silica gel, eluting with hexane: diethyl ether (1:1), to yield 339.3 grams of the desired product as a colorless oil.

-26-

Example 2

Preparation of
 α -(4-Hydroxyphenyl)- ω -hydroxypoly(oxybutylene)



A solution of 54.10 grams of the product from Example 1 in 100 mL of ethyl acetate and 100 mL of acetic acid containing 5.86 grams of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of solvent in vacuo followed by azeotropic removal of residual acetic acid with toluene under vacuum yielded 48.1 grams of the desired product as a colorless oil. The product had an average of 24 oxybutylene units. ^1H NMR (CDCl_3) δ 7.2 (broad s, 2H), 6.7 (s, 4H), 3.1-4.0 (m, 72H), 1.2-1.8 (m, 48H), 0.8 (t, 72H).

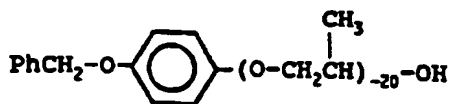
Similarly, by using the above procedures and the appropriate starting materials and reagents, the following compounds can be prepared:

- α -(2-hydroxyphenyl)- ω -hydroxypoly(oxybutylene);
- α -(3-hydroxyphenyl)- ω -hydroxypoly(oxybutylene);
- α -(3-*t*-butyl-4-hydroxyphenyl)- ω -hydroxypoly(oxybutylene);
- α -(4-hydroxy-3-methoxyphenyl)- ω -hydroxypoly(oxybutylene);
- α -(3,4-dihydroxyphenyl)- ω -hydroxypoly(oxybutylene);
- α -(3,4-hydroxy-5-methylphenyl)- ω -hydroxypoly(oxybutylene);
- α -(3,5-di-*t*-butyl-4-hydroxyphenyl)- ω -hydroxypoly(oxybutylene); and
- α -(3,4,5-trihydroxyphenyl)- ω -hydroxypoly(oxybutylene).

-27-

Example 3

Preparation of
 α -(4-Benzoyloxyphenyl)- ω -hydroxypoly(oxypropylene)

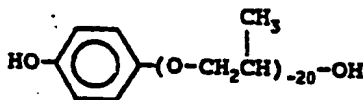


To a flask equipped with magnetic stirrer, thermometer, addition funnel, reflux condenser and nitrogen inlet was added 6.88 grams of a 35 wt % dispersion of potassium hydride in mineral oil. 4-Benzoyloxyphenol (40 grams) dissolved in 500 mL of anhydrous toluene was added dropwise and then stirred at room temperature for ten minutes. The temperature of the reaction mixture, a thick white suspension, was raised to 110°C and stirred for 3 hours. The reaction was cooled to room temperature and 349.9 mL of 1,2-epoxypropane was added dropwise. The reaction mixture was refluxed until the pot temperature reached 110°C (approximately 96 hours) at which time the reaction mixture was a light brown clear solution. The reaction was cooled to room temperature, quenched with 50 mL of methanol and diluted with 1 liter of diethyl ether. The reaction was washed with saturated aqueous ammonium chloride, followed by water and saturated aqueous sodium chloride. The organic layer was dried over anhydrous sulfate, filtered and the solvents removed under vacuum to yield 212.2 grams of the desired product as a light yellow oil.

-28-

Example 4

Preparation of

 α -(4-Hydroxyphenyl)- ω -hydroxypoly(oxypropylene)

A solution of 60.0 grams of the product from Example 3 in 100 mL of ethyl acetate and 100 mL of acetic acid containing 7.0 grams of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of solvent *in vacuo* followed by azeotropic removal of the residual acetic acid with toluene under vacuum yielded 31.7 grams of the desired product as a brown oil. The product had an average of 20 oxypropylene units. ^1H NMR (CDCl_3) δ 6.7 (s, 4H), 5.4-6.0 (broad s, 2H), 3.0-4.0 (m, 60H), 0.8-1.4 (m, 60H).

Similarly, by using the above procedures and the appropriate starting materials and reagents, the following compounds can be prepared:

- α -(2-hydroxyphenyl)- ω -hydroxypoly(oxypropylene);
- α -(3-hydroxyphenyl)- ω -hydroxypoly(oxypropylene);
- α -(4-hydroxy-3-methylphenyl)- ω -hydroxypoly(oxypropylene);
- α -(3,5-dimethoxy-4-hydroxyphenyl)- ω -hydroxy-poly(oxypropylene);
- α -(3,4-dihydroxyphenyl)- ω -hydroxypoly(oxypropylene);
- α -(3,5-di-*t*-butyl-4-hydroxyphenyl)- ω -hydroxy-poly(oxypropylene); and
- α -(3,4,5-trihydroxyphenyl)- ω -hydroxypoly(oxypropylene).

-29-

01

Example 5

02

03

Preparation of 2-(4-Benzylloxyphenyl)ethanol

04

05 To a flask equipped with a magnetic stirrer, reflux
 06 condenser and nitrogen inlet was added 13.8 grams of 2-(4-
 07 hydroxyphenyl)ethanol, 14.5 grams of anhydrous potassium
 08 carbonate, 33.0 grams of tetrabutylammonium bromide, 12 mL
 09 of benzyl chloride and 200 mL of acetone. The reaction
 10 mixture was heated at reflux for 3 days, and then cooled to
 11 room temperature and filtered. The filtrate was
 12 concentrated in vacuo, diluted with 500 mL of
 13 dichloromethane, and washed with 2% aqueous sodium hydroxide
 14 and then with saturated brine. The organic layer was dried
 15 over anhydrous magnesium sulfate, filtered, and concentrated
 16 in vacuo. The resulting product was purified by
 17 chromatography on silica gel, eluting with dichloromethane,
 18 to yield 20.0 grams of the desired product as a white solid.
 19

20

Example 6

21

22

Preparation of

23

 α -(2-(4-Benzylloxyphenyl)ethyl)- ω -hydroxypoly(oxybutylene)

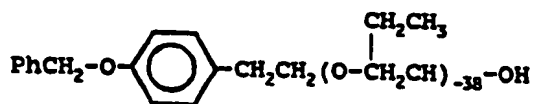
24

25

26

27

28



29

30

31

32

33

34

35

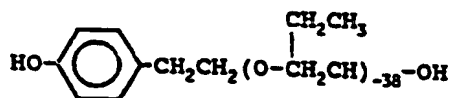
To a flask equipped with a magnetic stirrer, thermometer,
 addition funnel, reflux condenser and nitrogen inlet was
 added 1.05 grams of a 35 weight percent dispersion of
 potassium hydride in mineral oil and 50 mL of toluene.
 2-(4-Benzylloxyphenyl)ethanol (6.8 grams) from Example 5,
 dissolved in 7.5 mL of toluene, was added dropwise and the

01 mixture was heated at reflux for two hours. The reaction
02 was cooled to room temperature and 65 mL of 1,2-epoxybutane
03 were added dropwise. The reaction mixture was then refluxed
04 until the pot temperature reached 110°C (approximately 16
05 hours). The reaction was then cooled to room temperature,
06 quenched with 50 mL of methanol and diluted with diethyl
07 ether (300 mL). The organic layer was washed with water (2
08 times), saturated aqueous ammonium chloride (2 times), dried
09 over anhydrous magnesium sulfate, filtered and concentrated
10 in vacuo. The resulting product was chromatographed on
11 silica gel, eluting with hexane/diethyl ether, followed by
12 hexane/diethyl ether/ethanol (7.5:2.5:0.5) to yield 26.0
13 grams of the desired product as a colorless oil.

14
15 Example 7

16
17 Preparation of

18 α -(2-(4-Hydroxyphenyl)ethyl)- ω -hydroxypoly(oxybutylene)
19



26 A solution of 26.0 grams of the product from Example 6 in 50
27 mL of ethyl acetate and 50 mL of acetic acid containing 3.0
28 grams of 10% palladium on charcoal was hydrogenolyzed at 35-
29 40 psi for 16 hours on a Parr low-pressure hydrogenator.
30 Catalyst filtration and removal of solvent in vacuo followed
31 by azeotropic removal of residual acetic acid with toluene
32 under vacuum yielded 21.0 grams of the desired product as a
33 light yellow oil. The product had an average of 38
34 oxybutylene units. ¹H NMR (CDCl₃) δ 6.7, 6.9 (AB quartet,
35 4H), 3.0-3.8 (m, 116H), 2.75 (t, 2H), 0.6-1.8 (m, 190H).

-31-

01 Similarly, by using the above procedures and the appropriate
 02 starting materials and reagents, the following compounds can
 03 be prepared:

04

05 α -[2-(2-hydroxyphenyl)ethyl]- ω -hydroxypoly(oxybutylene);
 06 α -[2-(3-hydroxyphenyl)ethyl]- ω -hydroxypoly(oxybutylene);
 07 α -[3-(4-hydroxyphenyl)propyl]- ω -hydroxypoly(oxybutylene);
 08 α -[2-(3,4-dihydroxyphenyl)ethyl]- ω -hydroxypoly(oxybutylene);
 09 α -[3-(3,4-dihydroxyphenyl)propyl]- ω -hydroxy-
 10 poly(oxybutylene);
 11 α -[2-(3,5-di-t-butyl-4-hydroxyphenyl)ethyl]- ω -hydroxy-
 12 poly(oxybutylene); and
 13 α -[2-(3,4,5-trihydroxyphenyl)ethyl]- ω -hydroxy-
 14 poly(oxybutylene).
 15

16

Example 8

17

18

Preparation of

19

α -(4-Hydroxyphenyl)- ω -benzyloxypoly(oxybutylene)

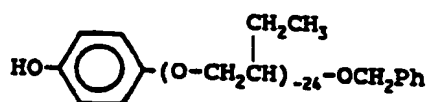
20

21

22

23

24



25

26

27

28

29

30

31

32

33

34

35

To a flask equipped with a magnetic stirrer, thermometer,
 reflux condenser and nitrogen inlet was added 0.8 grams of a
 35 wt % dispersion of potassium hydride in mineral oil. The
 oil was removed by trituration with anhydrous toluene. The
 product from Example 2 (6.0 grams) was dissolved in 50 mL of
 anhydrous tetrahydrofuran and added dropwise to the
 potassium hydride. The reaction mixture was heated to
 reflux for 45 minutes and then cooled to room temperature.
 Benzyl chloride (0.36 mL) was added dropwise and the
 reaction was then heated to reflux for 12 hours, cooled to

-32-

01 room temperature and quenched with 2 mL of isopropanol. The
02 solvent was removed in vacuo and the residue dissolved in
03 200 mL of diethyl ether, washed with 5% aqueous hydrochloric
04 acid followed by saturated aqueous sodium chloride. The
05 organic layer was dried over anhydrous magnesium sulfate,
06 filtered and the solvents removed under vacuum. The oil was
07 chromatographed on silica gel, eluting with hexane/ ethyl
08 acetate (7:3), to yield 3.8 grams of the desired product as
09 a colorless oil. The product had an average of 24
10 oxybutylene units. ¹H NMR (CDCl₃) δ 7.2-7.4 (m, 6H), 6.7
11 (s, 4H), 4.4-4.7 (m, 2H), 3.1-4.0 (m, 72H), 1.2-1.8 (m,
12 48H), 0.8 (t, 72H).

13

14 Similarly, by using the above procedures and the appropriate
15 starting materials and reagents, the following compounds can
16 be prepared:

17

18 α-(2-hydroxyphenyl)-ω-benzyloxypoly(oxybutylene);
19 α-(3-hydroxyphenyl)-ω-benzyloxypoly(oxybutylene);
20 α-(3,4-dihydroxyphenyl)-ω-benzyloxypoly(oxybutylene);
21 α-(3,5-di-t-butyl-4-hydroxyphenyl)-ω-benzyloxy-
22 poly(oxybutylene);
23 α-(4-hydroxy-3-methoxyphenyl)-ω-benzyloxy-
24 poly(oxybutylene); and
25 α-[2-(4-hydroxyphenyl)ethyl]-ω-benzyloxypoly(oxybutylene).

26

27

28

29

30

31

32

33

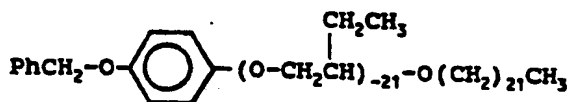
34

35

-33-

Example 9

Preparation of

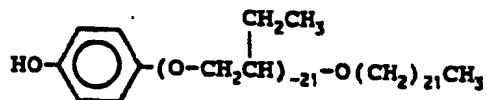
 α -(4-Benzoxyphehyl)- ω -docosanoxypoly(oxybutylene)

To a flask equipped with a magnetic stirrer, addition funnel, reflux condenser and nitrogen inlet was added 7.26 grams of a 35 wt % dispersion of potassium hydride in mineral oil. The oil was removed by trituration with anhydrous hexane, and 500 milliliters of anhydrous tetrahydrofuran were added. α -(4-Benzyloxyphenyl)- ω -hydroxypoly(oxybutylene) (104.0 grams) containing an average of 21 oxybutylene units (prepared essentially as described in Example 1), dissolved in 100 milliliters of anhydrous tetrahydrofuran, was added dropwise and the resulting mixture was heated to reflux for two hours. The reaction was then cooled to room temperature and 24.0 grams of 1-bromodocosane were added. The reaction was refluxed for sixteen hours, cooled to room temperature, diluted with 1200 mL of diethyl ether, and washed with 5% aqueous hydrochloric acid, followed by brine. The organic layers were dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to give an oil. The oil was chromatographed on silica gel, eluting with hexane/ethyl acetate (7:3) to yield 11.0 grams of the desired product as a yellow oil.

-34-

Example 10

Preparation of
 α -(4-Hydroxyphenyl)- ω -docosanoxypoly(oxybutylene)



A solution of 11.0 grams of the product from Example 9 in 50 mL of ethyl acetate and 50 mL of acetic acid containing 1.5 grams of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 14 hours on a Parr low-pressure hydrogenator. Catalyst filtration and removal of solvent *in vacuo* followed by azeotropic removal of the residual acetic acid with toluene under vacuum yielded 10.2 grams of the desired product. The product had an average of 21 oxybutylene units. ¹H NMR (CDCl₃) δ 6.7 (s, 4H), 3.1-4.0 (m, 62H), 0.6-1.8 (m, 148H).

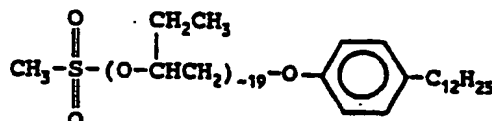
Similarly, by using the above procedures and the appropriate starting materials and reagents, the following compounds can be prepared:

- α -(4-hydroxyphenyl)- ω -n-butoxypoly(oxybutylene);
- α -(4-hydroxyphenyl)- ω -n-octyloxypoly(oxybutylene);
- α -(4-hydroxyphenyl)- ω -n-dodecyloxypoly(oxybutylene);
- α -(3,5-di-*t*-butyl-4-hydroxyphenyl)- ω -n-pentyloxy-poly(oxybutylene);
- α -(4-hydroxy-3-methoxyphenyl)- ω -n-hexyloxypoly(oxybutylene);
- α -(3,4-hydroxyphenyl)- ω -nonyloxypoly(oxybutylene); and
- α -[2-(4-hydroxyphenyl)ethyl]- ω -octyloxypoly(oxybutylene).

-35-

Example 11

Preparation of

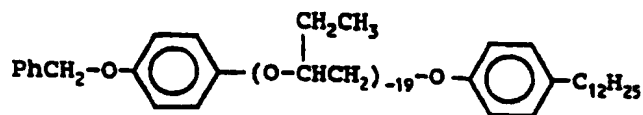
 α -(Methanesulfonyl)- ω -4-dodecylphenoxy poly(oxybutylene)

To a flask equipped with a magnetic stirrer, septa and a nitrogen inlet was added 35.0 grams of α -hydroxy- ω -4-dodecylphenoxy poly(oxybutylene) having an average of 19 oxybutylene units (prepared essentially as described in Example 6 of U.S. Patent No. 4,160,648), 440 mL of dichloromethane and 3.6 mL of triethylamine. The flask was cooled in an ice bath and 1.8 mL of methanesulfonyl chloride were added dropwise. The ice bath was removed and the reaction was stirred at room temperature for 16 hours. Dichloromethane (800 mL) was added and the organic phase was washed two times with saturated aqueous sodium bicarbonate, and then once with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to yield 35.04 grams of the desired product as a yellow oil.

-36-

Example 12

Preparation of

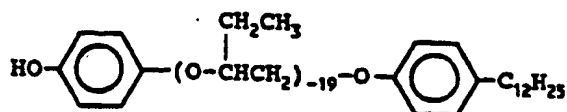
 α -(4-Benzoyloxyphenyl)- ω -4-dodecylphenoxypoly(oxybutylene)

To a flask equipped magnetic stirrer, reflux condenser, nitrogen inlet and septa was added 2.59 grams of a 35 wt % dispersion of potassium hydride in mineral oil. The mineral oil was removed by trituration with hexane and the flask was cooled in an ice bath. 4-Benzoyloxyphenol (4.11 grams) dissolved in 150 mL of tetrahydrofuran was added dropwise. The ice bath was removed and the reaction was allowed to stir for 45 minutes at room temperature. The mesylate from Example 11 was dissolved in 275 mL of anhydrous tetrahydrofuran and added to the reaction mixture. The resulting solution was refluxed for 16 hours, cooled to room temperature and 10 mL of methanol were added. The reaction was diluted with 1 liter of diethyl ether, washed with water (1 time), brine (1 time), dried over anhydrous magnesium sulfate, filtered and concentrated in vacuo to 36.04 grams of a yellow oil. The oil was chromatographed on silica gel, eluting with hexane/diethyl ether/ethanol (8:1.8:0.2) to yield 18.88 grams of the desired product as a light yellow oil.

-37-

Example 13

Preparation of

 α -(4-Hydroxyphenyl)- ω -4-dodecylphenoxy poly(oxybutylene)

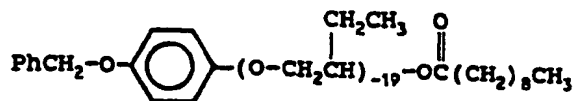
A solution of 18.88 grams of the product from Example 12 in 80 mL of ethyl acetate and 80 mL of acetic acid containing 2.08 grams of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 6 hours on a Parr low-pressure hydrogenator. Filtration of the catalyst and removal of solvent in vacuo, followed by azeotropic removal of residual acetic acid with toluene under vacuum yielded 17.63 grams of the desired product as a yellow oil. The product had an average of 19 oxybutylene units. 1H NMR ($CDCl_3$) δ 7.0-7.3 (m, 2H), 6.6-6.9 (m, 6H), 4.0-4.2 (m, 1H), 3.8-4.0 (m, 2H), 3.0-3.8 (m, 54H), 0.5-1.8 (m, 120H).

Similarly, by using the above procedures and the appropriate starting materials and reagents, the following compounds can be prepared:

- α -(2-hydroxyphenyl)- ω -4-dodecylphenoxy poly(oxybutylene);
- α -(3-hydroxyphenyl)- ω -4-dodecylphenoxy poly(oxybutylene);
- α -(3,4-dihydroxyphenyl)- ω -4-dodecylphenoxy poly(oxybutylene);
- α -(4-hydroxyphenyl)- ω -phenoxy poly(oxybutylene);
- α -(4-hydroxyphenyl)- ω -4-*t*-butylphenoxy poly(oxybutylene);
- α -(4-hydroxyphenyl)- ω -4-decylphenoxy poly(oxybutylene); and
- α -(4-hydroxyphenyl)- ω -4-octadecylphenoxy poly(oxybutylene).

Example 14

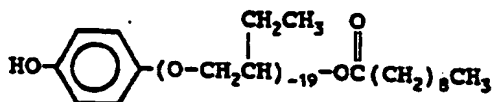
Preparation of

 α -(4-Benzoxyphehyl)- ω -decanoyloxypoly(oxybutylene)

α -(4-Benzoxyphehyl)- ω -hydroxypoly(oxybutylene) (40.75 grams) containing an average of 19 oxybutylene units (prepared essentially as described in Example 1) was combined with 200 mL of toluene, 3.9 mL of triethylamine, 1.5 grams of 4-dimethylamine pyridine and 5.2 mL of n-decanoyl chloride in a flask equipped with a thermometer, magnetic stirrer, reflux condenser and nitrogen inlet. The contents were refluxed for 16 hours, cooled to room temperature and diluted with 400 mL of hexane. The organic layers were washed with water (2 times), saturated aqueous sodium bicarbonate (2 times), saturated aqueous sodium chloride (2 times), dried over anhydrous magnesium sulfate, filtered and concentrated to yield 40 grams of a yellow oil. The oil was chromatographed on silica gel, eluting with hexane/diethyl ether (1:1) to yield 23.3 grams of the product as a yellow oil.

Example 15

Preparation of

 α -(4-Hydroxyphenyl)- ω -decanoyloxypoly(oxybutylene)

A solution of the ester from Example 14 (23.3 grams) in 50 mL of ethyl acetate and 50 mL of acetic acid containing 2.5 grams of 10% palladium on charcoal was hydrogenolyzed at 35-40 psi for 16 hours on a Parr low-pressure hydrogenator. Filtration of the catalyst and removal of solvent in vacuo followed by azeotropic removal of residual acetic acid with toluene under vacuum yielded 16.0 grams of the desired product as a yellow oil. The product had an average of 19 oxybutylene units. IR (neat) 1735 cm^{-1} ; ^1H NMR (CDCl_3) δ 6.7 (s, 4H), 4.8-4.9 (m, 1H), 3.1-4.0 (m, 56H), 2.3 (t, 2H), 0.7-1.8 (m, 112H).

Similarly, by using the above procedures and the appropriate starting materials and reagents, the following compounds can be prepared:

- α -(2-hydroxyphenyl)- ω -decanoyloxypoly(oxybutylene);
- α -(3-hydroxyphenyl)- ω -decanoyloxypoly(oxybutylene);
- α -(4-hydroxyphenyl)- ω -dodecanoyloxypoly(oxybutylene);
- α -(4-hydroxyphenyl)- ω -octanoyloxypoly(oxybutylene);
- α -(4-hydroxyphenyl)- ω -butanoyloxypoly(oxybutylene);
- α -(4-hydroxyphenyl)- ω -benzoyloxypoly(oxybutylene);
- α -(3,4-dihydroxyphenyl)- ω -hexanoyloxypoly(oxybutylene);
- α -(3,4-hydroxyphenyl)- ω -2-ethylhexanoyloxy-poly(oxybutylene);

-40-

- 01 α -(3,5-di-*t*-butyl-4-hydroxyphenyl)- ω -nonanoyloxy-
02 poly(oxybutylene);
03 α -(3,4,5-trihydroxyphenyl)- ω -decanoyloxy-
04 poly(oxybutylene); and
05 α -[2-(4-hydroxyphenyl)ethyl]- ω -decanoyloxypoly(oxybutylene).
06

07 Comparative Example A

08
09 Preparation of Polyisobutylphenol
10

11 To a flask equipped with a magnetic stirrer, reflux
12 condenser, thermometer, addition funnel and nitrogen inlet
13 was added 203.2 grams of phenol. The phenol was warmed to
14 40°C and boron trifluoride etherate (73.5 mL) was added
15 dropwise. Ultravis 10 polyisobutene (1040 grams, molecular
16 weight 950, 76% methylvinylidene isomer, available from
17 British Petroleum), dissolved in 1,863 mL of hexane, was
18 then added to the reaction mixture at a rate sufficient to
19 maintain the temperature between 22-27°C. The reaction
20 mixture was then stirred for 16 hours at room temperature.
21 Concentrated ammonium hydroxide (400 mL) was then added and
22 the mixture was diluted with 2 L of hexane. The resulting
23 mixture was washed with water (3 x 2 L), dried over
24 anhydrous magnesium sulfate, filtered and the solvent
25 removed *in vacuo* to yield 1,056.5 grams of an oil. This oil
26 was determined to contain 80% of the desired
27 polyisobutylphenol and 20% polyisobutene by ¹H NMR, and also
28 by chromatography on silica gel, eluting first with hexane
29 and then with hexane/ ethyl acetate/ethanol (93:5:2).
30
31
32
33
34
35

-42-

Table I
Single-Cylinder Engine Test Results

Sample ¹	Intake Valve Deposit Weight (in milligrams)		
	Run 1	Run 2	Average
Base Fuel	214.7	193.7	204.2
Example 2	12.7	26.5	19.6
Example 4	59.6	73.8	66.7
Example 7	44.3	54.0	42.9
Example 8	52.8	75.9	64.4
Example 10	53.9	47.9	50.9
Example 13	32.2	32.3	32.3
Example 15	32.5	31.1	31.8

¹ At 200 parts per million actives (ppma).

The base fuel employed in the above single-cylinder engine tests was a regular octane unleaded gasoline containing no fuel detergent. The test compounds were admixed with the base fuel to give a concentration of 200 ppma (parts per million actives).

The data in Table I illustrates the significant reduction in intake valve deposits provided by the poly(oxyalkylene) hydroxyaromatic ethers of the present invention (Examples 2, 4, 7, 8, 10, 13, 15) compared to the base fuel.

Example 17

Multicylinder Engine Test

The poly(oxyalkylene) hydroxyaromatic ethers of the present invention were tested in a laboratory multicylinder engine to evaluate their intake valve and combustion chamber

-43-

01 deposit control performance. The test engine was a 4.3
02 liter, TBI (throttle body injected), V6 engine manufactured
03 by General Motors Corporation.
04

05 The major engine dimensions are set forth in Table II:
06

07 Table II

08 Engine Dimensions

09		
10	Bore	10.16 cm
11	Stroke	8.84 cm
12	Displacement Volume	4.3 liter
13	Compression Ratio	9.3:1
14		

15 The test engine was operated for 40 hours (24 hours a day)
16 on a prescribed load and speed schedule representative of
17 typical driving conditions. The cycle for engine operation
18 during the test is set forth in Table III.

19 Table III

20 Engine Driving Cycle

21					
22	Step	Mode	Time in Mode, [Sec]	Dynamometer Load [kg]	Engine Speed [RPM]
23					
24	1	Idle	60	0	800
25	2	City Cruise	150	10	1,500
26	3	Acceleration	40	25	2,800
27	4	Heavy HWY Cruise	210	15	2,200
28	5	Light HWY Cruise	60	10	2,200
29	6	Idle	60	0	800
30	7	City Cruise	180	10	1,500
31	8	Idle	60	0	800
32					

33 ¹ All steps, except step number 3, include a 15 second
34 transition ramp. Step 3 includes a 20 second
35 transition ramp.

01 All of the test runs were made with the same base gasoline,
02 which was representative of commercial unleaded fuel. The
03 results are set forth in Table IV.
04

05 Table IV

06 Multicylinder Engine Test Results

Sample ¹		Intake Valve Deposits ²	Combustion Chamber Deposits ²
Base Fuel	Run 1	951	1887
	Run 2	993	1916
	Average	972	1902
Example 2	Run 1	266	2571
	Run 2	300	2522
	Average	283	2547
Comparative	Run 1	229	2699
Example A	Run 2	218	2738
	Average	224	2719

20 ¹ At 400 parts per million actives (ppma).
21 ² In milligrams (mg).
22

23 The base fuel employed in the above multicylinder engine
24 tests contained no fuel detergent. The test compounds were
25 admixed with the base fuel to give a concentration of 400
26 ppma (parts per million actives).
27

28 The data in Table IV illustrates the significant reduction
29 in intake valve deposits provided by the poly(oxyalkylene)
30 hydroxyaromatic ethers of the present invention (Example 2)
31 compared to the base fuel. Moreover, the data in Table IV
32 further demonstrates the significant reduction in combustion
33 chamber deposits produced by the poly(oxyalkylene)
34 hydroxyaromatic ethers of the present invention (Example 2)
35

-45-

01 compared to a known polyisobutylphenol fuel additive
02 (Comparative Example A).
03
04
05
06
07
08
09
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35

-46-

01 WHAT IS CLAIMED IS:

02

03 1. A compound of the formula:

04

05

06

07

08

09

10

11

12

or a fuel-soluble salt thereof; wherein

13

14

15

16

R_1 and R_2 are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

17

18

19

R_3 and R_4 are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

20

21

22

23

R_5 is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group of the formula:

24

25

26

27

28

29

30

31

32

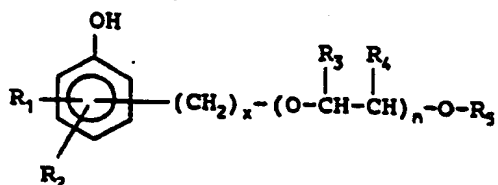
wherein R_6 is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms;

33

34

35

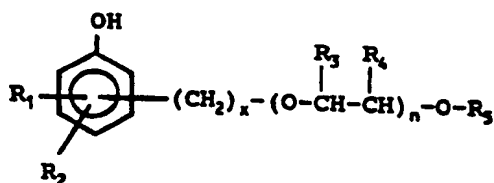
n is an integer from 5 to 100; and x is an integer from 0 to 10.



- 01 2. The compound according to Claim 1, wherein n is an
02 integer ranging from 10 to 50.
03
- 04 3. The compound according to Claim 2, wherein n is an
05 integer ranging from 15 to 30.
06
- 07 4. The compound according to Claim 2, wherein R₁ is
08 hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon
09 atoms; and R₂ is hydrogen.
10
- 11 5. The compound according to Claim 4, wherein R₃ is
12 hydrogen, alkyl having 2 to 22 carbon atoms,
13 alkylphenyl having an alkyl group containing 4 to 24
14 carbon atoms, or an acyl group having the formula:
15 -C(O)R₇, wherein R₇ is alkyl having 4 to 12 carbon
16 atoms.
17
- 18 6. The compound according to Claim 5, wherein R₁ is
19 hydrogen or hydroxy.
20
- 21 7. The compound according to Claim 6, wherein R₃ is
22 hydrogen, alkyl having 4 to 12 carbon atoms, or
23 alkylphenyl having an alkyl group containing 4 to 12
24 carbon atoms.
25
- 26 8. The compound according to Claim 7, wherein one of R₃
27 and R₄ is lower alkyl having 1 to 3 carbon atoms and
28 the other is hydrogen.
29
- 30 9. The compound according to Claim 8, wherein one of R₃
31 and R₄ is methyl or ethyl and the other is hydrogen.
32
- 33 10. The compound according to Claim 9, wherein x is 0, 1 or
34 2.
35

-48-

- 01 11. The compound according to Claim 10, wherein R_1 and R_2
 02 are both hydrogen, and x is 0.
 03
- 04 12. A fuel composition comprising a major amount of
 05 hydrocarbons boiling in the gasoline or diesel range
 06 and an effective detergent amount of a compound of the
 07 formula:
 08



16 or a fuel-soluble salt thereof; wherein

17

18 R_1 and R_2 are each independently hydrogen, hydroxy,
 19 lower alkyl having 1 to 6 carbon atoms, or lower alkoxy
 20 having 1 to 6 carbon atoms;

21

22 R_3 and R_4 are each independently hydrogen or lower
 23 alkyl having 1 to 6 carbon atoms;

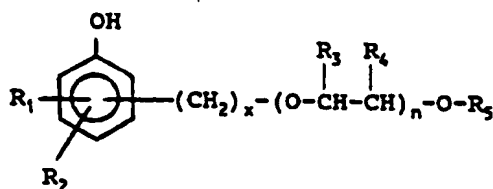
24

25 R_5 is hydrogen, alkyl having 1 to 30 carbon atoms,
 26 phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms,
 27 or an acyl group of the formula:



33 wherein R_6 is alkyl having 1 to 30 carbon atoms,
 34 phenyl, or aralkyl or alkaryl having 7 to 36 carbon
 35 atoms;

- 01 n is an integer from 5 to 100; and x is an integer from
 02 0 to 10.
 03
- 04 13. The fuel composition according to Claim 12, wherein R₁
 05 is hydrogen, hydroxy, or lower alkyl having 1 to 4
 06 carbon atoms; R₂ is hydrogen; one of R₃ and R₄ is
 07 hydrogen and the other is methyl or ethyl; R₅ is
 08 hydrogen, alkyl having 2 to 22 carbon atoms,
 09 alkylphenyl having an alkyl group containing 4 to 24
 10 carbon atoms, or an acyl group having the formula:
 11 -C(O)R₇, wherein R₇ is alkyl having 4 to 12 carbon
 12 atoms; n is 15 to 30 and x is 0, 1 or 2.
 13
- 14 14. The fuel composition according to Claim 13, wherein R₁
 15 is hydrogen or hydroxy; R₂ is hydrogen, alkyl having 4
 16 to 12 carbon atoms, or alkylphenyl having an alkyl
 17 group containing 4 to 12 carbon atoms; and x is 0.
 18
- 19 15. The fuel composition according to Claim 14, wherein R₁
 20 and R₂ are both hydrogen.
 21
- 22 16. The fuel composition according to Claim 12, wherein
 23 said composition contains about 50 to about 2500 parts
 24 per million by weight of said compound.
 25
- 26 17. A fuel concentrate comprising an inert stable
 27 oleophilic organic solvent boiling in the range of from
 28 about 150°F to 400°F and from about 10 to about 70
 29 weight percent of a compound of the formula:
 30



or a fuel-soluble salt thereof; wherein

R_1 and R_2 are each independently hydrogen, hydroxy, lower alkyl having 1 to 6 carbon atoms, or lower alkoxy having 1 to 6 carbon atoms;

R_3 and R_4 are each independently hydrogen or lower alkyl having 1 to 6 carbon atoms;

R_5 is hydrogen, alkyl having 1 to 30 carbon atoms, phenyl, aralkyl or alkaryl having 7 to 36 carbon atoms, or an acyl group of the formula:



wherein R_6 is alkyl having 1 to 30 carbon atoms, phenyl, or aralkyl or alkaryl having 7 to 36 carbon atoms;

n is an integer from 5 to 100; and x is an integer from 0 to 10.

18. The fuel concentrate according to Claim 17, wherein R_1 is hydrogen, hydroxy, or lower alkyl having 1 to 4 carbon atoms; R_2 is hydrogen; one of R_3 and R_4 is hydrogen and the other is methyl or ethyl; R_5 is hydrogen, alkyl having 2 to 22 carbon atoms, alkylphenyl having an alkyl group containing 4 to 24 carbon atoms, or an acyl group having the formula: $-\text{C}(\text{O})\text{R}_7$, wherein R_7 is alkyl having 4 to 12 carbon atoms; n is 15 to 30 and x is 0, 1 or 2.

-51-

01 19. The fuel concentrate according to Claim 18, wherein R₁
02 is hydrogen or hydroxy; R₂ is hydrogen, alkyl having 4
03 to 12 carbon atoms, or alkylphenyl having an alkyl
04 group containing 4 to 12 carbon atoms; and x is 0.
05

06 20. The fuel concentrate according to Claim 19, wherein R₁
07 and R₂ are both hydrogen.
08
09
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/12320

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C10L 1/18, 10/00; C07C 43/11, 43/18, 43/20, 69/00, 69/76

US CL : 44/400, 442, 443; 560/109, 144; 568/607, 608, 609, 611

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/400, 442, 443; 560/109, 144; 568/607, 608, 609, 611

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,024,678 (MERTENS-GOTTSELIG ET AL.) 18 JUNE 1991 (SEE ENTIRE DOCUMENT)	1-20
Y	US, A, 2,213,477 (STEINDORFF ET AL.) 03 SEPTEMBER 1940 (PAGE 1, LEFT COLUMN, LINES 1-34; PAGE 1, RIGHT COLUMN, LINES 17-33)	1-11
Y	US, A, 2,984,553 (ANDRESS) 16 MAY 1961 (COLUMN 2, LINE 60 TO COLUMN 3, LINE 6)	1-11
Y	US, A, 4,191,537 (LEWIS ET AL.) 04 MARCH 1980 (COLUMN 10, LINES 38-40)	17-20
Y	UK, A, 708,193 (THOMPSON PRODUCTS, INC.) 28 APRIL 1954 (PAGE 1, LINES 16-39)	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

15 March 1994

Date of mailing of the international search report

MAR 25 1994

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. NOT APPLICABLE

Authorized officer

JERRY D. JOHNSON

Telephone No. (703) 308-0661